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(Substitute Specification - Marked-Up Version)

AUSTENITIC NICKEL-CHROMIUM-MOLYBDENUM-SILICON ALLOY WITH HIGH CORROSION RESISTANCE TO HOT CHLORIDE-CONTAINING GASES AND CHLORIDE

[0001] The invention relates to an austenitic nickel-chromium-molybdenum-silicon alloy with additions of silicon.

[0002] In plants and aggregates where hot chlorine-containing gases and chloride-containing deposits occur (chemical plants, thermal waste-disposal facilities, in particular when recycling special waste, plants for the recycling of biomass, large diesel engines, exhaust systems of automobiles) ferritic boiler construction steel is used at temperatures up to 400 °C. At higher temperature, nickel-chromium-molybdenum alloys with 21.5% chromium, 9% molybdenum, 3.7% niobium 2.5% iron, and the remainder nickel and unavoidable impurities (German material number 2.4856) are used (steel code 1995)

[0003] [However, the] <u>The</u> alloy with the material number 2.4856 is <u>however</u> difficult to process. [Furthermore] <u>In addition</u> this alloy suffers a considerable ductility loss at temperatures above 500 °C, a loss which may result in the formation of cracks in pressure-carrying components

and/or those subjected to heavy mechanical stress. To a certain extent, the start of precipitation of the ductility-reducing precipitation [precipitants] can be delayed by lowering the iron content.

[0004] Measures leading to a clear rise in ductility are indicated in the international patent application WO 95/31579 in which a new alloy is described on basis of the alloy according to material number 2.4856 which [that] distinguishes itself through increased hot and cold formability and a greater ductility.

[0005] [Also the] The new alloy described in this publication still has some disadvantages. Thus the indicated ductility-raising measures cause the corrosion resistance to gases containing great amounts of chlorine and coatings containing chloride to drop below that of alloy with the material number 2.4856. Already with this alloy, high corrosion rates occur for reasons of constantly rising process and exhaust gas temperatures due to the increase in effectiveness. Alloys of the type 2.4856 are [furthermore] in addition subject to heat corrosion by [sulfate] sulphate-containing deposits, so that a considerable need for an alloy of a different type, with improved resistance to high-temperature corrosion exists.

[0006] JP-A 6199649 discloses an alloy for electrically conductive rollers whose essential alloy components (in weight percentages) are indicated as follows: Cr 15 - 30%, Mo 4 - 10%, Si $\leq$ 2 , Fe $\leq$ 10 %, Mn $\leq$ 2 %, Al 0.2 - 2 % and Ti 0.05 - 2 %. Alternatively, Niob can also

be used instead of Titan in the above-mentioned distribution.

[0007] WO-A 8901985 discloses a corrosion-resistant cast alloy which (in weight %) contains essentially the following alloy components: Cr 20 - 25 %, Mo 6 - 9 %, Si 05 - 1 %, Fe 15 - 20 % and Mn 2 - 4 %. In addition a high addition of Co, in the amount of 4 - 8% is indicated.

[0008] It is the object of present invention to develop an alloy with a resistance to chlorine [chloric] gas corrosion and to chloride-containing coatings [clearly in proved over] significantly superior to that of the state of the art, while [having] at the same time [better] providing increased resistance to [sulfate] sulphate corrosion [and a] while possessing high ductility over the entire temperature range up to 1000°C.

[0009] [This] The object is attained by means of a silicon-containing nickel-chromium-molybdenum alloy which is made up of the following components (in mass %):

Cr	18 - 22 %
Mo	6 - 10 %
Si	0.6 - 1.7 %
C	0.002 - 0.05 %
Fe	1 - 5 %
Mn	0.05 - 0.5 %
Al	0.1 - 0.5 %
Ti	0.1 - 0.5 %
Mg	0.005 - 0.05 %

Ca	0.001 - 0.01 %
V	max. 0.5 %
P	max. 0.02 %
S	max. 0.01 %
B	0.001 - 0.01 %
Cu	max. 0.5 %
Co	max 1 %
Nb	max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth elements - 0.02 - 0.5%

the remainder being nickel and impurities caused by the melting process, whereby the total amount of additions in Nb + Al + Ti do not exceed 1 %.

[0010] Advantageous further developments of the object of the invention are to be found in the sub-claims.

[0011] The alloy according to the invention is clearly more high-temperature corrosion resistant to [high temperature corrosion from] chlorine-containing gases, [chlorine] chloride-containing ash[es], deposits and salt compounds [combinations] than those of [in] the state of the art, while [being] at the same time being corrosion resistant to [sulfate] sulphate corrosion and wet corrosion [while remaining] and is at the same time highly ductile.

[0012] [Advantageous further developments of the object of the invention are to be found in the sub-claims.]

[0013] A preferred alloy is composed of [characterized by] the following alloy

components (in mass percentages) :

Cr	18 - 20 %
Mo	8 - 9.0 %
Si	0.7 - 1.1 %
C	0.002 - 0.15 %
Fe	2.5 - 3.5 %
Mn	0.05 - 0.1 %
Al	0.1 - 0.3 %
Ti	0.1 - 0.4 %
Mg	0.005 - 0.15 %
Ca	0.001 - 0.005 %
V	max. 0.1 %
P	max. 0.002 %
S	max. 0.001 %
B	0.001 - 0.001 %
Cu	max. 0.5 %
Nb	max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth elements - 0.03 - 0.06%
the remainder being nickel and impurities caused by the melting process.

[0014] The alloy is advantageously suited on the one hand for the production of pipes, in particular composite pipes, sheet metal, band material, [films] foils, wires as well as [articles] items made from these semi-[finished]products, and [on the other hand for build-up] is furthermore suitable as corrosion protection in form of applied welding or plating [of applied corrosion protection].

[0015] The advantageous [properties] characteristics of the alloy according to the invention [become apparent from the] appear in the following examples of embodiments

[indicated below]. Table 1 shows [the] for example [of] analyses of [charges from] batches of the alloy [(A-f)]according to the invention (A-F) as well as the comparison alloys (G, H) [with components outside] other than the combination according to the invention (G, H). [For comparison, the] The alloy 2.4856 was used for comparison. All alloy variants [of the alloy] were produced from cast blocks by means of hot rolling followed by cold rolling at room temperature.

[0016] The resistance of the alloy according to the invention to chloride corrosion [appears from the] is depicted in Figs. 1 and 2. For the tests, polished and cleaned test coupons of different test alloys were [dipped into] submerged in an aqueous solution of 1 mol/l NaCl, 0.1 mol/l $CaCl_2$ and [0.24] 0.25 mol/l $NaHCO_3$, [were] dried at 60°C and then aged in the air at 750°C [air temperature] for 240 hours. This test simulates the stresses which appear [such as occur] e.g. in exhaust systems of car [automobile] engines (at [on expansion] bellows for [the] uncoupling [of] catalytic converter and engine). Fig. 1 shows the disappearance of [he] metal [loss], Fig. 2 shows the metallographically determined corrosion effect [damage determined through metallography] at the end of the test. In [these investigations] tests it was found [that] surprisingly that the resistance to chloride corrosion could be markedly improved [considerably e.g.] over that of [the] alloy 2,4856 by [adding] the addition of silicon in quantities from 0.6 and 1.7%.

[0017] The advantageous influence of silicon can also be seen [becomes apparent] in Fig. 3 which shows the metallographically determined corrosion [damage of] effect on samples [determined through metallography, said samples having been placed into] which were aged in a complex medium (chlorine-containing synthetical waste combustion gas (2.5 g/m^3 $HC1$, 1.3 g/m^3 SO_2/ 9% O_2, the remainder [N_s] N_2) [with simultaneous subjection to] while at the same time adding chloride-containing boiler ash) for over 1000 hours at 600°C. By comparison [Compared] with the [charge containing little silicon] low-silicon batch (e.g. G) the [silicon-containing] alloy containing silicon according to the invention [suffers distinctly] suffered markedly less corrosion [attack] effect.

[0018] Fig. 4 shows the corrosion [damage] effect after a cyclic 1008 [hours of cyclical] hour aging of samples which [had been] were coated [with a coating consisting of Na_2SO_4/KCl] before aging at 750° C in a chlorine and sulfur dioxide-containing atmosphere with a coat of $Na_2SO_4/KC1$. This test serves to test [the] resistance to sulphate corrosion. As can be seen in the figure, the degrees of corrosion in the alloys according to the invention [has clearly] are markedly lower [corrosion rates] also with this corrosion stress [exposure to corrosion] than the alloy 2,4856 used at this time under such corrosion conditions [of corrosion].

[0019] The outstanding characteristics of the alloy according to the invention can be attributed to the silicon additions and to the coordination of the alloy elements molybdenum,

[chrome] chromium and iron. The silicon contents of the alloy according to the invention should be [from] between 0.6 [to] and 1.7 %, since the corrosion-[resistant] inhibiting effect of [the] silicon no longer occurs with lower silicon contents[,] and since [greater contents of silicon result in the appearance of] embrittling silicides and a [distinct] marked loss [of] in ductility, in particular at middle temperatures [in the middle range] (500 - 800°C) are to be expected with higher contents in silicon. With silicon contents [from] between 0.5 [to] and 1.7 % the [notched] notch bar [impact value] test toughness, measured [on] in ISO-V [notched bar samples] Charpy tests, does not drop below 100 J/cm as shown in Fig. 5, even after aging for 1000 hours [aging] at 600°C [, as shown in Fig. 5].

[0020] The molybdenum content of the alloy according to the invention is limited to 10% [since] because, as shown in Fig. 4, the [risk] vulnerability to [sulfate] sulphate corrosion increases with [higher] molybdenum contents. A minimum molybdenum [Molybdenum] content is [necessary] required in order to avoid wet corrosion in case of [falling short of] a drop below the dew point.

[0021] The [chrome] chromium content of the alloy according to the invention should be between 18% and 22% in order to ensure sufficient corrosion resistance. Greater [Higher chrome] contents in chromium render the workability of nickel-[chrome]chromium-molybdenum alloys [distinctly] markedly more difficult.

[0022] [In addition, the] The alloy should furthermore contain hafnium and/or rare earth elements and/or zirconium and/or yttrium if an improved [adhesion] adherence of protective oxide layers is required in case of rapid temperature changes for specific applications, e.g. in [the] automobile exhaust systems [at high temperatures and/or in case of rapid temperature changes]. [The] However the sum of these reactive elements should [however] not exceed 0.5%.

[0023] The iron content[s] of the alloy according to the invention is limited to a maximum of 5%, [since] as the danger that slightly volatile iron chlorides may be produced exists in case of higher iron contents [involve the danger of easily volatile iron chlorides being formed]. A minimum iron content of 1% is however required in order to ensure the workability of the alloy.

[0024] The carbon content of the alloy according to the invention is limited to a maximum 0.05% [as higher carbon contents involve the risk] because of the danger of intercrystalline corrosion in case of higher carbon contents.

[0025] The contents of titanium and aluminum [contents] are limited for either [respectively] to a maximum of 0.5%[;] and the actually undesirable contents of niobium [is limited] to a maximum of 0.5% [because] as these elements may [result in] lead to a loss of ductility at medium temperatures [due to] because of the formation of intermettallic phases. The

total sum of additions of niobium, aluminum and titanium [additives] should not exceed 1%. A minimum content in oxygen-[affinitive]refined elements aluminum, titanium, magnesium and calcium is however necessary in order to ensure good [resistance to] oxidation resistance. The contents in manganese [content] should be at least 0.05% for processing reasons, but should not exceed 0.5% because higher [contents in] manganese contents adversely affect [have an unfavorable effect on] the oxidation resistance [to oxidation]. In order to [To] improve workability, 0.001 to 0.01% boron are also added [into the mix] to the alloy.

[0026] The contents in phosphor and sulfur [contents] should be kept as low as possible, as [because] these [surface] interfacially active elements lower [reduce] the high-temperature corrosion resistance [at high temperature] as well as the ductility of the alloy.

[0027] The alloy according to the invention can be used for bands, [films] foils, [sheet metals] sheets, pipes (seamless or welded), wires, [for applied welding, applied] as application weldment, as application plating or as composite piping.

[0028] The production of the alloy according to the invention [can be produced by ingot] may be effected by means of block casting [as well as by] or also continuous casting after [following] melting in a vacuum induction furnace or after open melting. The [Recasting of the] alloy [is possible] may be remelted but this is not absolutely necessary. Hot-forming is

[achieved] effected by forging, hot rolling or [continuous pressing and] extruder, while cold forming is effected by cold rolling, wire pulling or [by means of] putting through a pilger mill. The production of [composite] combination materials, e.g. plating on carbon steel, can be [effected] done by means of one of the [customary] conventional application welding processes, [by] through cold or hot rolling of [sheet metal] sheets or bands, [by] through explosive cladding or [bu] through one of the [customary] conventional processes for [in] the production of bimetal pipes.

[0029] Thanks [Due] to its excellent resistance to chlorination, the alloy is especially [well suited as] suitable in form of band [and] or sheet [metal], pipe or plating material for utilization in hot, chorine-containing gases, or in the presence of chloride-containing coatings, such as occur in chemical industrial plants, in plants for the thermal treatment [plants for] of chlorine-containing chemical waste and contaminated [floors] soil as well as in [automobile] car exhaust gas systems ([expansion] bellows for the uncoupling of exhaust catalytic converter and engine). The excellent resistance of the alloy to complex corrosive [saline] salt deposits (boiler [furnace] ash) renders the alloy also suitable for the utilization as plating and construction material in plants for thermal waste removal [removal plants], in large diesel engines [motors], in plants for the obtention of energy from biomass and in plants of the cellulose industry.

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CLAIMS

1. Austenitic nickel-chromium-molybdenum alloys with [additives] additions of silicon, characterized by alloy components (in mass percentages) :

Cr	18 - 22 %
Mo	6 - 10 %
Si	0.6 - 1.7 %
C	0.002 - 0.05 %
Fe	1 - 5 %
Mn	0.05 - 0.5 %
Al	0.1 - 0.5 %
Ti	0.1 - 0.5 %
Mg	0.005 - 0.05 %
Ca	0.001 - 0.01 %
V	max. 0.5 %
P	max. 0.02 %
S	max. 0.01 %
B	0.001 - 0.01 %
Cu	max. 0.5 %
Co	max 1 %
Nb	max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth elements - 0.02 - 0.5%
the remainder being nickel and impurities caused by the melting process, whereby the total amount of additions in Nb + Al + Ti do not exceed 1 %.

2. Alloy as in claim 1, characterized by alloy components (in mass percentages):

Cr	18 - 20 %
Mo	8 - 9.0 %
Si	0.7 - 1.1 %
C	0.002 - 0.15 %
Fe	2.5 - 3.5 %
Mn	0.05 - 0.1 %
Al	0.1 - 0.3 %

Ti	0.1 - 0.4 %
Mg	0.005 - 0.15 %
Ca	0.001 - 0.005 %
V	max. 0.1 %
P	max. 0.002 %
S	max. 0.001 %
B	0.001 - 0.001 %
Cu	max. 0.5 %
Nb	max. 0.5 %

Hf and/or Y and/or Zr and/or rare earth elements - 0.03 - 0.06%
the remainder being nickel and impurities caused by the melting process.

3. Alloy as in claim 1, characterized by a molybdenum content between 6.5 and 9.5 %

4. Alloy as in claim 1, characterized by a silicon content between 0.6 and 1.3 %

5. Utilization of the alloy as in one of the claims 1 to 4, for the production of pipes, sheet metal, band material, [films] foils, wires as well as of [articles] items made of these semi-[finished]products.

6. Utilization of the alloy [as in] according to one of the claims 1 to 4 for the production of composite pipes.

7. Utilization of the alloy according to the invention as in one of the claims 1 to 4 as corrosion protection in form of applied [by means of bulid-up] welding or plating.